Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

Esterification of oleic acid for biodiesel production catalyzed by 4-dodecylbenzenesulfonic acid

Alexandra Alegría, Jorge Cuellar*

Department of Chemical Engineering, University of Salamanca, Plaza de los Caídos 1-5, 37008 Salamanca, Spain

ABSTRACT

The esterification of oleic acid with methanol by homogeneous acid catalysis was investigated, using 4-dodecylbenzenesulfonic acid as catalyst. First, the catalytic activity of 4-dodecylbenzenesulfonic acid in this reaction was compared with that of *p*-toluenesulfonic and sulfuric acid, and it was found that the reaction rate clearly increased with increasing hydrophobicity of the catalyst. Second, the effects of the catalyst/acid molar ratio, the methanol/oleic acid molar ratio, the water content, temperature, the stirring speed and the presence of triglycerides on the kinetics and the equilibrium of this esterification were studied. The main observations were that temperature and the proportion of catalyst had a positive effect on the kinetics, i.e., an increase in any of these factors led to an increase in the reaction rate. Methanol had an almost negligible effect. By contrast, water had a negative effect due to the formation of an aqueous phase, which removed part of the catalyst, thus reducing its concentration in the organic phase and hence the reaction rate. Third, the kinetics of esterification was studied in a wide range of operating conditions and a reversible second-order model was obtained that included the effect of the separation of the aqueous phase from the reaction mixture and hence the progressive decrease in the concentration of catalyst, methanol and the volume of the reaction mixture. This kinetic model adequately predicts the experimental data within the range of operation conditions investigated. The activation energy for the forward reaction was 58.5 kJ/mol, and 63.4 kJ/mol for the reverse reaction.

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1. Introduction

Organic esters are of considerable economic interest due to their applications as solvents, extractants, plasticizers, lubricants, lubricant additives and even, in the case of some volatile esters, as aromatic compounds in perfumes, cosmetics and foods [1]. Thus, any progress made in esterification methodology can be of considerable economic importance. In particular, study of the esterification of fatty acids with short-chain alcohols is of utmost importance owing to the presence, in noteworthy proportions, of this type of carboxylic acid in the low-cost oils/fats used as raw materials for the production of "second generation" biodiesel. In this particular case, the need for the study arises because when low-cost raw materials, such as waste cooking oils/fats [2,3] or inedible oils [4,5], are used in the production of biodiesel with a basic catalyst, their high content in fatty acids (up to 40% in some cases [3]) leads to the formation of soaps, which greatly increases product separation costs.

To circumvent this problem, the esterification of the fatty acids present in these low-cost raw materials has been studied in depth using different types of liquid and solid catalysts [6–10]. One of the best known solutions is probably the synthesis of biodiesel in two steps: in a first step, the fatty acids are esterified using an acid catalyst and, in the second step, triglycerides are transesterified using a basic catalyst [11–14]. However, a two-step process increases the fixed and operating costs and hence the overall costs of the process of obtaining biodiesel.

There is therefore no doubt regarding the economic transcendence that the achievement of both esterification and transesterification in a single step using an acid catalyst would have. In the search for this short cut, the first obstacle to be overcome is finding a suitable acid catalyst. The usual inorganic catalysts, such as sulfuric acid, are not appropriate because they are highly polar and hence the rate of transesterification is very slow owing to the preferential location of the catalyst in the alcoholic phase. In this phase, there is only a very low concentration of triglycerides because of the low miscibility of triglycerides in the alcoholic phase. This low concentration of triglycerides in the alcoholic phase leads to a slow overall reaction rate because the reaction rate is controlled by the mass transfer rate between the two phases [15].

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* Corresponding author. Tel.: +34 923294479.
  E-mail address: cuellar@usal.es (J. Cuellar).

Accordingly, in an attempt to avoid the drawbacks of liquid inorganic acid catalysts, the use of solid catalysts is currently being investigated, bearing in mind mainly the economic advantage provided by its easier separation from the reaction mixture than in the case of liquid catalysts. In this respect, most solid acid catalysts studied are functionalized inorganic oxides such as modified zirconia (sulfated or tungstated zirconia) [16], zeolites [17] or supported heteropolyacids [18], but to date solid catalysts, either acid or basic, have shown serious disadvantages: they need high temperatures to work properly; the reaction rate is slow because the reactants have to move within the solid catalyst by diffusion mechanisms; and, furthermore, catalyst deactivation occurs [19,20].

However, there is an alternative catalytic pathway that has not been sufficiently explored. This involves the use of alkyl-benzenesulfonic organic acids as catalysts in esterification and transesterification reactions. In this case, an aromatic ring linked to a long alkyl chain endows the acid catalyst with an amphiphilic nature and thus provides higher solubility in the oil phase. As a result, since the solubility of the alcohol in the oily phase is significantly higher than that of triglycerides in the alcoholic phase, the rate of the transesterification reaction is much faster than with inorganic acid catalysts. Sulfonic-type catalysts have mainly been studied in solid form (catalytic functional groups attached to a porous solid support), such as cation exchange resins [21,22], ordered mesoporous silica (SBA-15) containing sulfonic groups [23,24], and sulfonated carbon-based catalysts [25]. However, the problems with this type of catalyst are the same as those referred to above: high temperatures are necessary, the reaction rate is slow due to the mass transfer of reactants by diffusion and, in some cases, the formation of fines and a loss of catalytic groups may occur.

Nevertheless, a promising alternative is the use of a liquid amphiphilic acid catalyst. In this sense, studies carried out with 4-dodecylbenzenesulfonic acid (DBSA) have shown that this acid catalyzes the transesterification reaction, and even the esterification of FFAs added to oils, very efficiently. At 90 °C, this catalyst allows conversions of triglycerides and FFAs to biodiesel close to 100% to be achieved in about 2 h, using methanol/oil or methanol/fatty acid ratios below twice the stoichiometric amount [15]. This acid is commercially available and is reasonably affordable (≈€3/kg). Also, since it is used in a small proportion relative to the oil, in cases in which it cannot be recovered, only €0.02/L is added to the cost of the biodiesel. Moreover, this catalyst does not have the drawbacks of solid or inorganic acid catalysts.

Therefore, considering that according to the reported data DBSA is an excellent catalyst in transesterification reactions, and, in particular, has a proven capacity to simultaneously catalyze both esterification and transesterification reactions [15], it seems entirely appropriate to conduct a thorough investigation aimed at determining its behavior in FFA esterification reactions under very different experimental conditions.

In this respect, the first objective of the present research was to compare the behavior of this catalyst with those of others catalysts in esterification reactions. Second, a more specific and important goal was the generation of the information necessary for the design of processes for obtaining biodiesel from raw materials with high contents of FFAs and water. Bearing this in mind, in this work the effectiveness of DBSA as a catalyst for the esterification of oleic acid with methanol was studied by determining the effects of the following variables on the kinetics and equilibrium of esterification: the catalyst/fatty acid molar ratio, the methanol/fatty acid molar ratio, the initial water/oleic acid weight ratio, temperature, the stirring speed, and the effect of the presence of triglycerides.

Furthermore, a kinetic equation of the esterification reaction that is able to predict the conversion of oleic acid over a broad range of operating conditions reasonably well was determined. This equation considers that the reaction is of first order with respect to

each of the four components of the reaction mixture and that the decreasing catalyst and methanol concentrations play an important role in the kinetics because of their water solubility and the fact that the organic and aqueous phases are separated.

2. Experimental

2.1. Materials

Oleic acid (>97%, Fluka, Spain) and methanol (>99.8%, Scharlau, Spain) were used as reactants for the esterification experiments. The catalysts tested were DBSA (mixture of isomers, ≥95%, Sigma–Aldrich, Spain), p-toluenesulfonic acid monohydrate (98%, Sigma-Aldrich, Spain) and concentrated sulfuric acid (95–97%, Scharlau, Spain). A solution of potassium hydroxide (>85%, Scharlau, Spain) in ethanol (>99.5%, Scharlau, Spain) was used as the titrant solution in the analysis of the reaction mixture. Refined sunflower seed oil (Sovena, Spain) was used to study the effect of the presence of triglycerides on the esterification reaction. All reagents were used as received, without further purification.

2.2. Procedure for the esterification of oleic acid

Oleic acid methyl esters were synthesized from the esterification of oleic acid with methanol, using DBSA as catalyst. All the experimental conditions are given in Table 1. For each experiment, the predetermined proportions of acid and catalyst were first mixed in a 5 mL reactor (a glass flask with a screw cap), which was immersed in a thermostat bath to attain the predetermined operation temperature. Then, the required amount of methanol was added to the reactor. This time was considered as the zero reaction time. The reactant mixture was stirred at 600 rpm using a Teflon-coated magnetic stir-bar. The progress of the reaction was measured by analyzing the amount of oleic acid remaining in the reaction mixture by titration with a solution of potassium hydroxide in ethanol. To prevent any methanol loss due to evaporation in each sampling, instead of using a single reactor per set of experimental conditions, each set of experimental conditions was replicated a number of times equal to the predetermined number of samples to be taken for their analysis; that is, the reaction was carried out in at least eight reactors for each set of experimental conditions, and the amount of unreacted oleic acid remaining in each reactor was determined at a different time.

Prior to the analysis of the reaction mixture in each reactor by acid-base titration, the corresponding reactor was removed from the thermostatic bath and immediately transferred to an ice bath to quench the reaction.

The conversion of oleic acid (X) was determined using the expression:

$$X(\%) = \frac{a_0 - a_t}{a_0} \times 100 \tag{1}$$

where a_0 is the initial (at t_0) acidity (the number of oleic acid moles in the reactor) and a_t is the acidity at time t.

2.3. Experimental planning

The objective of this study was mainly to determine the influence of the operating conditions on the kinetics and on the equilibrium of the esterification of oleic acid with methanol. Although to our knowledge DBSA has not been used so far in this type of reaction, the esterification of many carboxylic acids has already been addressed by different authors and hence the variables that influence the kinetics and equilibrium of the reaction are well known: temperature (T), the catalyst/fatty acid molar ratio (Cat), the methanol/fatty acid molar ratio (Met), the initial

Table 1
Operation conditions of the experimental plan for the esterification of oleic acid with methanol.

Study number	Experimental study		Operation conditions			
			T (°C)	Cat[a]	Met[a]	H_2O[b]
1	Activity of the catalyst	– No catalyst	60	–	2:1	0:1
2		–H_2SO_4	60	0.015:1	2:1	0:1
3		– p-TSA	60	0.015:1	2:1	0:1
4		– DBSA	60	0.015:1	2:1	0:1
5	Effect of the Cat factor		60	0.005:1	2:1	0:1
6			60	0.010:1	2:1	0:1
7			60	0.015:1	2:1	0:1
8			60	0.020:1	2:1	0:1
9	Effect of the Met factor		60	0.015:1	2:1	0:1
10			60	0.015:1	4:1	0:1
11			60	0.015:1	6:1	0:1
12			60	0.015:1	8:1	0:1
13	Effect of the H_2O factor		60	0.015:1	2:1	0:1
14			60	0.015:1	2:1	0.01:1
15			60	0.015:1	2:1	0.05:1
16			60	0.015:1	2:1	0.10:1
17	Effect of the T factor		60	0.005:1	2:1	0:1
18			60	0.010:1	2:1	0:1
19			60	0.015:1	2:1	0:1
20			70	0.005:1	2:1	0:1
21			70	0.010:1	2:1	0:1
22			70	0.015:1	2:1	0:1
23			80	0.005:1	2:1	0:1
24			80	0.010:1	2:1	0:1
25			80	0.015:1	2:1	0:1
26	Presence of triglycerides in the reaction mixture		80	0.010:1	2:1	0:1

[a] Molar ratio.
[b] Weight ratio.

water/fatty acid weight ratio (H_2O) and the stirring rate [26–29]. Accordingly, in this work we studied the influence of all these variables and, additionally, the influence of the presence of triglycerides in the reaction mixture.

In a first set of preliminary experiments, the esterification of oleic acid was studied, with DBSA as catalyst, by varying the stirring speed from 0 to 800 rpm, while keeping constant the value of all the other operation conditions. The first finding was that when the mixture of reactants was subjected to vigorous stirring for a very short time at the beginning of the reaction, the stirring speed during the rest of the reaction time had negligible influence on the kinetics. Thus, apparently all the experiments could have been made without stirring. Nevertheless, to avoid any influence of the mass transfer rate on the reaction kinetics, a stirring speed of 600 rpm was established for all experiments.

Regarding the other variables, the operating conditions were chosen taking into account the range of values of the experimental conditions under which the transesterification reaction had been studied previously using this catalyst [15]. This choice was justifiable because the main interest of this work was to determine the experimental conditions under which it would be possible to achieve maximum fatty acid conversion, so that such information could be applied to the design of the experimental conditions to be used in the process of obtaining biodiesel from low-cost oils or fats. However, considering that esterification reactions are faster than transesterification reactions, some experimental conditions were milder than those in which transesterification was studied. This was mainly to prevent the esterification kinetics from being so fast that the monitoring of its evolution during the first minutes of the reaction would not be safe.

All experimental conditions are shown in Table 1. In a previous work, the experiments with transesterification reactions were performed with Cat values (which in the reference was the catalyst/oil molar ratio) between 0.03:1 and 0.09:1 [15]. Taking into account those values, and the fact that triglycerides contain 3 fatty acid chains, the equivalent Cat ratios in the esterification reaction should have values between 0.01:1 and 0.03:1. However, the study of the effect of the Cat variable was carried out with values from 0.005:1 to 0.020:1 to avoid excessively fast kinetics.

Study of the influence of the Met variable was performed with values of this factor between 2:1 and 8:1. Since an excess of alcohol over the stoichiometric ratio (1:1 ratio) is needed to shift the equilibrium towards the formation of the methyl ester, the 1:1 ratio was discarded. The higher values of Met were used to extract conclusions about its effect on equilibrium. It is worth mentioning here that these Met values are much lower than those used in other studies with sulfuric acid as catalyst, in which the optimum ratio was 60:1 [26].

Study of the influence of the initial water ratio, H_2O, was carried out with values of the water/oleic acid weight ratio between 0:1 and 0.10:1.

The influence of temperature was studied by carrying out esterification at three different temperatures: 60, 70 and 80 °C. The use of 90 °C was avoided because the kinetics would have been very fast and large errors could have occurred in the determination of the progress of the reaction. Another reason was to prevent the build-up of excessive pressure in the reactor, since the experimentation was performed in sealed glass reactors.

For each temperature, the reaction was carried out with at least three values of Cat to obtain enough experimental data to obtain a kinetic model that would include the Cat variable.

Finally, the kinetics of the esterification of oleic acid in the presence of triglycerides in the reaction mixture with DBSA as a catalyst was studied.
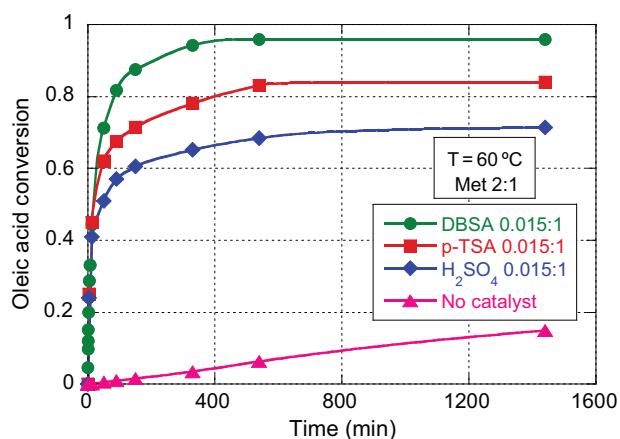
Fig. 1. Catalytic activity of DBSA, p-TSA and H$_2$SO$_4$ in the esterification of oleic acid (dots represent experimental data and solid lines have been drawn by interpolating between each pair of dots).

3. Results and discussion

3.1. Catalytic activity of DBSA in oleic acid esterification

Some acids, such as sulfuric or p-toluenesulfonic (p-TSA), are not considered suitable as catalysts for the transesterification of triglycerides with methanol owing to their low effectiveness as catalysts. However, these acids are frequently used in the esterification of fatty acids [26,28–32], and their application in the synthesis of biodiesel from raw materials with high FFA contents is also possible when the overall process consists of two steps [12–14].

Consequently, the first stage of this work involved a comparative study of the catalytic activity of sulfuric acid, p-TSA and DBSA in the esterification of oleic acid with methanol, in all cases under the same operating conditions (given in Table 1, experiments 1–4). The results are shown in Fig. 1, where it can be observed that the non-catalyzed esterification rate was very slow and that the fastest esterification was achieved using DBSA as catalyst.

The different results for the three homogeneous catalysts can be attributed, at least in part, to their different miscibility in oleic acid. Taking into account that water is generated as a reaction product in the esterification reaction, and that this water forms a second phase separated from the organic phase, a partitioning of the catalyst between the organic and aqueous phases occurs. Consequently, the more hydrophobic the catalyst, the greater the proportion of it that remains in the organic phase (in which the reaction is assumed to occur) and the smaller the proportion that passes into the aqueous phase. In the case of DBSA, its molecular structure contains a long hydrophobic aliphatic chain, which affords it better miscibility with oleic acid than in the case of the other catalysts and, additionally, hinders its passage to the aqueous phase. This explanation would account for the fact that the kinetics with DBSA is faster than with p-TSA and, in turn, that the kinetics with p-TSA is faster than with sulfuric acid.

The results of several previous studies that have used solid catalysts with attached sulfonic groups (several ion-exchange resins and amorphous carbon with sulfonic groups) are shown in Table 2. Although it is not possible to make comparisons, because the operating conditions are quite different (generally the T, Cat and Met values are higher than those used here with DBSA), it may be seen that in all cases the reaction rates are much lower than those obtained with DBSA. According to Andrijanto et al. [33], the results for D5081 resin are similar to those observed for DBSA regarding kinetics for a reaction time of 2 h, but in that process the authors used very high proportions of methanol (44:1) and, moreover, no

information was provided about whether conversions higher than 85% could be attained.

The conclusion to be drawn from the information concerning the catalytic activity of different acid catalysts is that not only does DBSA have a much higher catalytic activity in the transesterification of triglycerides than other acid catalysts, but also that DBSA has a higher catalytic activity than sulfuric acid, p-TSA and several solids with acid sulfonic groups in the esterification of fatty acids. Thus, this catalyst appears to be a good candidate for the transesterification of triglycerides with high levels of FFAs in a single step.

Regarding the corrosive potential of DBSA on process equipment, in the scientific literature we have found no information in this respect, but it is reasonable to expect that it should be lower than that of p-toluenesulfonic or sulfuric acid, since its long alkyl chain renders it less soluble in the aqueous phase, where the corrosive effect occurs, and, mainly, because the negatively charged 4-dodecylbenzenesulfonic anion can attach to the positively charged metallic surface of the process equipment via electrostatic forces, acting like a blocking barrier to inhibit corrosion [35].

Regarding recovery of the DBSA catalyst at the end of the esterification reaction, there are several alternatives. In one of them, the catalyst in the aqueous phase can be concentrated and reused, and the catalyst in the ester phase can be neutralized with sodium or calcium carbonate and filtered. In its sodic form (sodium dodecylbenzenesulfonate) the catalyst is an important cleaning agent in laundry detergents. The ester can be purified by washing with water after evaporation of the excess methanol.

In view of the good results obtained in this first test of the activity of DBSA, the second phase of this study was logically the determination of the effects of each of the operating conditions on the equilibrium conversion and on the kinetics of oleic acid esterification.

3.2. Effect of stirring speed

As stated in Section 2.3, after observing that the kinetics was barely affected by the stirring speed it was decided to perform all experiments of this work at 600 rpm.

3.3. Effect of the Cat value on equilibrium and kinetics

The experimental conditions for studying the effect of the Cat value on the equilibrium conversion and on the kinetics are given in Table 1, (experiments 5–8). The experimental results are shown in Fig. 2.

Fig. 2 shows that within the range of Cat values studied an increase in the proportion of catalyst leads to an increase in the reaction rate and that this effect is more pronounced in the initial moments of the reaction, as expected. However, a much more important observation was that the final conversion with the four proportions of catalyst was the same, i.e., the proportion of catalyst did not influence the equilibrium conversion.

The explanation accounting for these effects of the catalyst is straightforward. According to the Arrhenius equation, which relates the reaction rate constant to the activation energy of a reaction, a catalyst increases the reaction rate because it allows the reaction to proceed through the formation of intermediate compounds that require a lower activation energy for their formation than in the case of the non-catalyzed reaction. According to Lotero et al. [36], the mechanism of the esterification reaction by acid catalysis consists of several stages. The first, and key, step involves protonation of the oxygen of the carbonyl group, thus increasing the electrophilicity of the carboxyl carbon. Then, a nucleophilic attack of the alcohol occurs on that carbon, forming a tetrahedral

Table 2
Comparison of the results obtained in the esterification of fatty acids using different solid catalysts with attached sulfonic groups with those obtained using DBSA.

Fatty acid	Catalyst	T (°C)	Cat[a]	Met	Reaction time (h)	X (%)	Reference
Oleic acid	D5081	65	0.014:1	44:1	2	85	[33]
Oleic acid	Amberlist 15	65	0.066:1	44:1	2	45	[33]
Oleic acid	Relite CFS	85	0.027:1[b]	5.1:1[b]	3.3	80	[34]
Stearic acid	EBD-100	120	0.02:1[b]	2.1:1[b]	24	100[c]	[20]
Oleic acid	Amorphous carbon with SO_3H groups	95	0.088:1	25.8:1	4	99.9	[25]
Oleic acid	DBSA	60	0.015:1	2:1	5.5	96	This work

[a] For solid catalysts Cat = moles of SO_3H groups/mol fatty acid.

[b] In those works, fatty acids were esterified in the presence of an oil. Although the authors considered that oil behaves as an inert compound, the fact is that -albeit at a very slow rate in comparison with the esterification speed- the oil is also involved in the process and is transesterified. Accordingly, in this table Cat and Met were calculated considering the total fatty acid chains, whether as fatty acid or as triglycerides.

[c] Process in which water is removed.
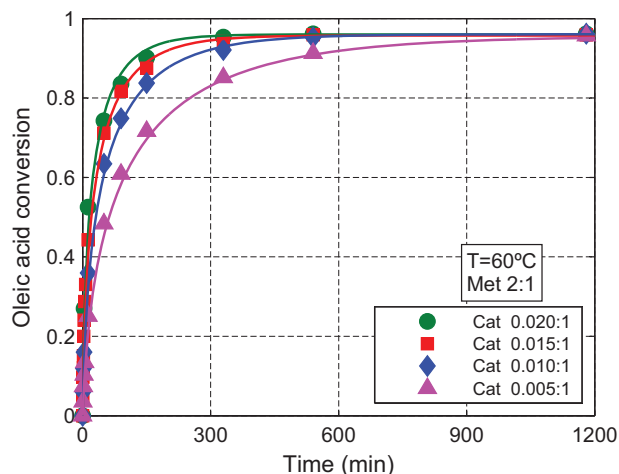
Fig. 2. Effect of the Cat value on the kinetics of the esterification of oleic acid with DBSA as catalyst.

intermediate. Finally, proton migration and a breakdown of the intermediate occur. Consequently, a higher proportion of catalyst increases the rate of formation of the intermediates and hence the overall rate of conversion of fatty acids.

Therefore, the conclusion is that the higher the amount of catalyst, the greater the availability of protons in the reaction mixture, which increases the rate of formation of the intermediate and hence the overall reaction rate. Accordingly, the higher the proportion of catalyst the sooner the equilibrium conversion will be reached, but the proportion of catalyst does not influence the final conversion.

3.4. Effect of the Met value on the equilibrium and kinetics

In reversible reactions, equilibrium conversion can be increased by adding an excess of one of the reactants. Thus, in the production of biodiesel from triglycerides and methanol it is usual to add methanol at a molar ratio 6:1 relative to triglycerides -that is, twice the stoichiometric amount- to shift the equilibrium to the right and also to increase the reaction rate due to the increased concentration of one of the reactants. With this objective in mind, in this work experiments were carried out with different values of the Met factor to quantify the effect of this factor on the kinetics and on equilibrium conversion in the esterification reaction of oleic acid with methanol. The experimental conditions are shown in Table 1, experiments 9–12. The results are shown in Fig. 3a–b, respectively.

The results, shown in Fig. 3a, indicate that the importance of the value of the proportion of methanol decreases as the conversion increases.

Regarding the equilibrium conversion of the reversible reaction, Fig. 3b shows its evolution when the value of Met is changed. Here, it can be noted that the higher the methanol excess, the higher
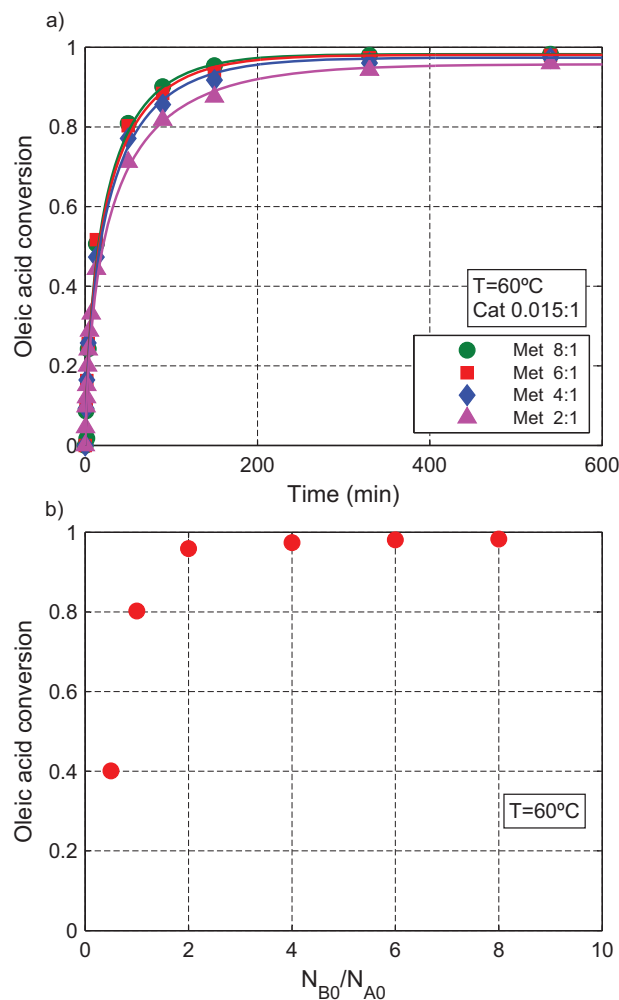
Fig. 3. Effect of the Met factor on the esterification of oleic acid with DBSA as catalyst: (a) on the kinetics; (b) on the equilibrium conversion.

the conversion, although this increase was negligible when the values of Met were higher than 2. In contrast, when the value of Met was the stoichiometric one, i.e., 1:1, the equilibrium conversion decreased significantly. The small difference between among the equilibrium conversions achieved with Met values ≥2 can be explained in terms of the notion that once a high level of conversion has been achieved, the water generated -even though it is a reaction product- only shifts the equilibrium of the reaction to the left slightly because it forms a separate phase.

The conclusion to be drawn from these results is that in the esterification reaction of oleic acid with methanol using DBSA as catalyst, owing to the separation of water as a second separate
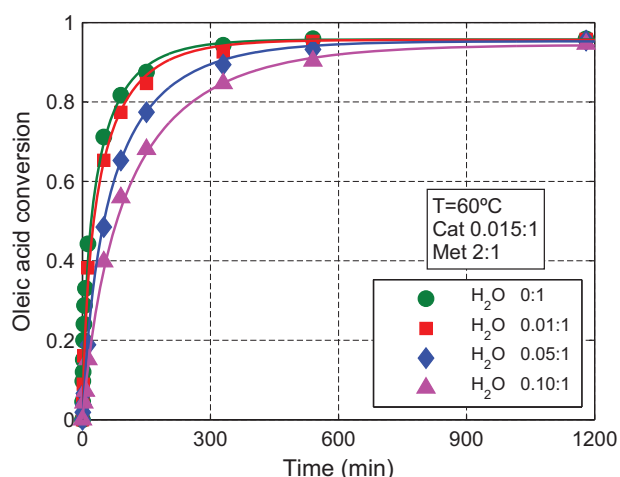
Fig. 4. Effect of the water/oleic acid weight ratio on the esterification of oleic acid with DBSA as catalyst.

phase it is not necessary to add high proportions of methanol to displace the equilibrium to achieve conversions close to 100%. This conclusion can be extrapolated to the case of the transesterification of low-cost triglycerides with high contents in FFAs, because the esterification takes place simultaneously with the transesterification of triglycerides, and in this case the glycerol produced also forms a second phase along with the water and thus enables the development of the esterification reaction until almost 100% conversion.

3.5. Effect of water on the equilibrium and kinetics

The esterification reaction is reversible and one of its products is water, such that the existence of water in raw materials may affect the shape of the curve of the reaction kinetics for three potential reasons: (i) the rate of the reverse reaction increases and hence the net reaction rate will be lower; (ii) the higher the initial proportion of water in the reaction mixture, the lower the conversion of fatty acids at the point of equilibrium, and (iii) if the water initially present, or that generated during the reaction, forms an aqueous phase, the catalyst may partially pass into the aqueous phase and thus decrease the reaction rate due to a decrease in the catalyst concentration in the organic phase, which is where the fatty acid is located.

Consequently, to determine the possible importance of the presence of water in the reaction mixture, the kinetics of the esterification reaction of oleic acid with different proportions of water was studied. The experimental conditions used to study the effect of the initial proportion of water in the reaction mixture on the equilibrium and on the kinetics of esterification are shown in Table 1, experiments 13–16, and the results of the experiments are shown in Fig. 4.

Fig. 4 shows that the higher the initial water proportion in the oleic acid, the slower the reaction rate. It also shows that the proportion of water has a negligible effect on the equilibrium conversion. The decrease in the reaction rate may be due to any combination of causes **i** and **iii** referred to in the first paragraph of this section although, given that the equilibrium conversion does not change with the proportion of water, effect **iii** is probably the most important reason for these results regarding the kinetics and the equilibrium; if some proportion of the catalyst passes into the aqueous phase, the catalyst concentration in the organic phase will decrease, and hence the reaction rate decreases. Additionally, if most of the water generated, or added, is separated as a second phase, its effect on the equilibrium conversion could become neg-

ligible. This explanation is consistent with the effects observed: the higher the proportion of water, the more catalyst passes to the aqueous phase and therefore the more the reaction rate decreases, while the equilibrium is scarcely modified because most of the water is located in the aqueous phase.

The extraction of the catalyst from the organic phase by water can be justified considering that, due to their basicity, water molecules solvate the protons of the catalyst, resulting in fewer protons being available to catalyze the reaction and, consequently, in a decrease in the "effective" concentration of catalyst [37]. Other authors have also found an inhibiting effect of water in esterification [29,31,38] and transesterification reactions [39], using catalysts such as sulfuric acid and p-TSA. In these cases the effect of water is much stronger than with DBSA, which may be explained by taking into account that the solubility of these catalysts in water is higher than that of DBSA, which is an amphiphilic substance. Unfortunately, it is not possible to make an in-depth comparison of the effect of water in esterification or transesterification reactions using DBSA and other catalysts, because the above works only give the results of the effect of water on the conversion at fixed reaction times. This is because in those works the authors merely reported that the reaction rate was slower, without clearly specifying whether the reaction had reached equilibrium or whether the final conversion reached was the same with or without the presence of water.

3.6. Effect of temperature on the equilibrium and kinetics

In irreversible reactions, an increase in temperature will usually result in an increase in the reaction rate, and the magnitude of the effect of temperature on the reaction rate, which can be quantified with the Arrhenius equation, depends on the activation energy. However, the effect of temperature in reversible reactions is more complex since temperature increases the kinetic coefficients of the forward and backward reactions. Hence, at the beginning of the reaction an increase in the reaction temperature will result in an increase in the net reaction rate due to the negligible importance of the backward reaction because of the low concentration of the reaction products. However, with the progress of the reaction, the net reaction rate increases or decreases, depending on the magnitude of the variation of the kinetic coefficients of the forward and backward reactions with temperature, and this variation is a function of the magnitude of the activation energy for each of these reactions. Since the difference between the activation energies for both reactions is equal to the reaction heat, it may be concluded that the magnitude of the variation in the net rate of the esterification reaction due to increasing the temperature depends on whether the reaction is endothermic or exothermic and on the value of the heat of reaction. In sum, by analyzing the theoretical variations of the values of the kinetic coefficients of the forward and reverse reactions with temperature, it can be concluded that in a reversible endothermic reaction the net reaction rate will always increase with increasing temperature and that equilibrium will be reached at higher conversions. By contrast, in a reversible exothermic reaction the net rate of reaction increases with increasing temperature but equilibrium is attained at lower conversions.

In this regard, the theoretical reaction heat of the esterification of oleic acid can be calculated from the heats of formation of the chemical species involved.
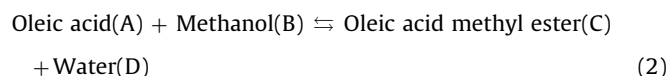
Taking into account that the reaction is:

Oleic acid(A) + Methanol(B) $\leftrightarrows$ Oleic acid methyl ester(C)

$\quad$ + Water(D) $\hspace{8cm}$ (2)

Table 3
Standard enthalpies of formation of the compounds involved in the esterification reaction of oleic acid.

Compound	H_f^0(kJ/mol)	Reference
Oleic acid	−764.8	[40]
Methanol	−239.5	[41]
Methyl oleate	−727.64	[42]
Water	−285.83	[43]

The heat of reaction, ΔH_r^0, can be calculated with the following equation:

$$\Delta H_r^0 = H_{fC}^0 + H_{fD}^0 - H_{fA}^0 - H_{fB}^0 = -9.17\text{kJ/mol} \qquad (3)$$

where $H_{f_i}^0$ denotes the standard values of the enthalpy of formation for the reactant or product i, which are given in Table 3. The value calculated for ΔH_r^0 indicates that the esterification reaction is slightly exothermic.

The results of our experiments are shown in Fig. 5, where it can be seen that with increasing temperature the reaction rate increased and the equilibrium conversion decreased, although this latter only very slightly.

Accordingly, the theoretical calculations and the experimental results indicate that the reaction is exothermic. However, the theoretical value of the reaction heat is very small and any minor error in the determination of the enthalpies of formation of the reaction components could have led to a positive result (endothermic reaction). Furthermore, the experimental evidence for the exothermicity of the reaction is very weak because the difference in conversion with temperature is almost negligible and the influence of the separation of water in a second phase in the equilibrium conversion must also be considered. If the solubility of water in the organic phase is increased by increasing temperature, an increased reaction temperature would favor an increase in the concentration of water in the organic phase and consequently the displacement of the equilibrium of the reaction to the left, thereby decreasing the conversion. The conclusion is that the small decrease in the conversion observed experimentally with increasing temperature cannot be attributed with certainty to the exothermicity of the reaction.

The results found in the literature also seem to disagree about whether the reaction is exothermic or endothermic. Thus, in some works it was found that the esterification reaction of fatty acids was endothermic, with a very low reaction heat (between 7 and 20 kJ/mol) [27,29,30,44,45], whereas there is apparently only one work that reports an exothermic esterification reaction, with a reaction heat of −11.1 kJ/mol [9].

Despite the foregoing, and taking into account that the reactions catalyzed by sulfuric or p-toluenesulfonic acid are very slow, and therefore that the advance toward equilibrium in the kinetic curve is very slow, it is possible that the determination of the endothermicity of the reaction may have been obtained from data on conversions lower that the true equilibrium conversions since, in these cases, higher temperatures lead to higher conversions.

Considering these problems, to study the influence of temperature on the kinetics and equilibrium, the esterification of oleic acid using DBSA as a catalyst was carried out at three different temperatures: 60, 70 and 80 °C. All other experimental conditions can be found in Table 1, experiments 17–25. Fig. 5 shows the results of these experiments.

3.6.1. Kinetic model

Optimizing the design of the processes of transesterification of triglycerides containing FFAs, or of processes of esterification of fatty acids, makes it necessary to have a kinetic equation for the esterification reaction that will allow the prediction of FFA conversion over time under various operating conditions. Several authors
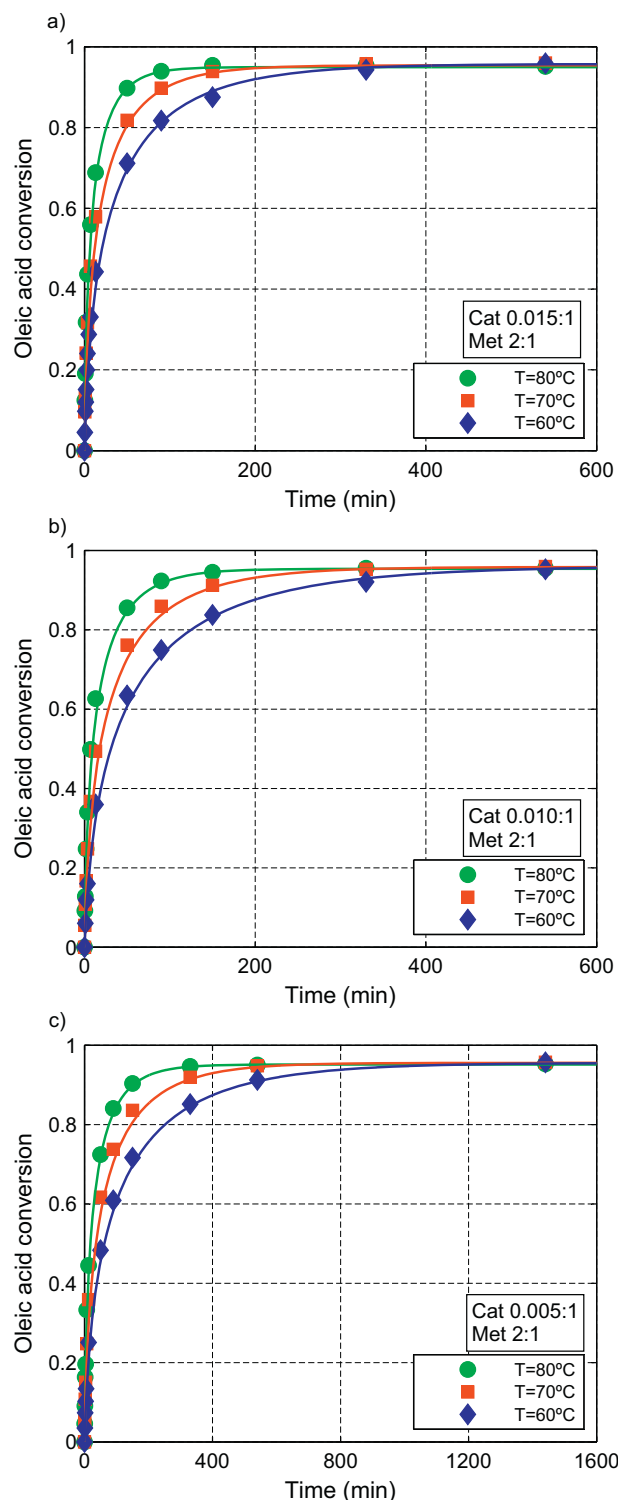

Fig. 5. Effect of temperature on the esterification of oleic acid with DBSA as catalyst.

have investigated the kinetics of the esterification of short chain carboxylic acids [38,46,47] and of the esterification of fatty acids contained in the oils for the production of biodiesel [9,29,32,44].

In those works, it was always considered that the esterification reaction was reversible and, in most of them, it was assumed that the reaction kinetics was of first order for each of the components of the reaction mixture; that is, that both the forward and reverse reactions were second order.

However, in the case of the esterification of fatty acids, the fitting of a simple kinetic model to the experimental data does not lead to satisfactory results across the whole range of conversions, probably due to variation in the concentrations of some of the components of the reaction mixture because the water generated during the reaction forms an aqueous phase separated from reaction mixture. This (the separation of water in a second phase) has already been reported in the case of the esterification of myristic acid [28].

Water separation adds complexity to the design of a kinetic model for the following reasons: (a) the water concentration in the reaction mixture, which is the organic phase, cannot be quantified in terms of conversion alone, because most of the water is in the aqueous phase; (b) the aqueous phase removes, at least partially, any hydrophilic catalyst from the organic phase, such that the effective catalyst concentration in the organic phase gradually decreases with the progress of the conversion of fatty acid; (c) the aqueous phase also removes methanol from the organic phase, and therefore the methanol concentration in the organic phase cannot be quantified either as a function of conversion alone; and (d) the existence of two separate phases opens the possibility, in some experimental conditions, for the reaction rate to be controlled by the rate of mass transfer between phases.

Considering that water decreases the net rate of esterification to a greater extent than what would be expected due to the increase in the reverse reaction rate, caused by its increasing concentration, Liu et al. [38] reported a kinetic equation for the esterification of acetic acid with sulfuric acid as catalyst, which includes a decrease in the catalytic activity of sulfuric acid with conversion due to the solvation of the protons of the catalyst by the water formed during the reaction. However, in that work, the esterified carboxylic acid was acetic acid, and hence no phase separation as clear as in the case of fatty acids occurred. Accordingly, there was no change in the volume of the reactant mixture, nor a decrease in the methanol concentration due to its transfer to the aqueous phase.

Consequently, in an attempt to obtain a kinetic equation for the esterification of fatty acids with a wide range of applicability here we propose a kinetic equation that includes the effect of the separation of the aqueous phase from the reaction mixture, and hence the progressive decrease in the concentration of the catalyst, methanol and the volume of the reaction mixture. Thus, the model is able to predict the oleic acid conversion over a broad range of operation conditions, including different reaction temperatures and proportions of catalyst, methanol and initial water.

In order to establish a realistic kinetic model, the first step was to explore the physicochemical phenomena involved in the esterification reaction and, under these assumptions, build a mathematical model. Following this approach, it should be noted that at the beginning of the reaction, provided that there is no excess of water, there is a homogeneous system, since oleic acid and methanol are miscible. As the reaction proceeds, the water generated exceeds its solubility in the organic phase and, initially, water droplets are formed. Finally, the water forms an aqueous phase that captures part of the methanol and part of the catalyst, such that the reactant mixture then becomes a heterogeneous system and hence, in the overall kinetics, mass transfer phenomena could be involved.

Accordingly, in view of the complexity of the kinetics of the esterification of fatty acids reactions, the modeling of the real phenomena is a difficult and fruitless task because the number of adjustable parameters in the model would be so high that their values would not be reliable since more than one set of values of the parameters could lead to the same results.

Consequently, the model was developed according to the following assumptions:

a) The speed of the uncatalyzed reaction is negligible with respect to the catalyzed reaction.
b) The reaction is reversible.
c) In view of the results concerning the effects of the factors, it is considered that the kinetic equation should include the concentrations of all the components of the reaction mixture, including the catalyst.
d) The reaction kinetics is considered to be of first order with respect to each of the reactants and products; i.e., it is of second order for the forward and reverse reactions.
e) The effective volume of the reaction mixture is the volume of the organic phase, since this is where the reaction occurs. This volume decreases with time due to the formation of an aqueous phase.
f) The catalyst concentration in the organic phase decreases progressively owing to its transfer to the aqueous phase. A distribution of the catalyst between the two phases is assumed.
g) The concentration of methanol also decreases as conversion advances because the water extracts the methanol from the organic phase.
h) The mass transfer steps are not included in the model so as not to include an excessive number of parameters in the model. It is therefore assumed that these phenomena do not affect the kinetics because they do not control the reaction rate.

The esterification reaction can be represented as:

$$A + B + Cat \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C + D + Cat \tag{4}$$
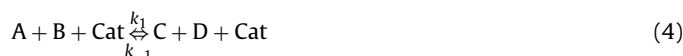
where A represents oleic acid, B, methanol, C, methyl oleate, D, water and Cat, the catalyst. Moreover, k_1 is the forward reaction rate constant and k_{-1} is the backward reaction rate constant.

Thus, the kinetics equation can be expressed as:

$$(r_C) = \frac{dC_C}{dt} = k_1 C_A C_B C_{Cat} - k_{-1} C_C C_D C_{Cat} \tag{5}$$

where C_i denotes the concentration of the compound i.

The kinetics equation can be also expressed in terms of the number of moles of each component in the reaction and of the organic phase volume.

$$\frac{dN_C}{dt} = k_1 \times \frac{N_A \times N_B \times N_{Cat}}{V_{org}^2} - k_{-1} \times \frac{N_C \times N_D \times N_{Cat}}{V_{org}^2} \tag{6}$$

where N_i is the number of moles of the compound i and V_{org} is the organic phase volume.

Now, taking into account the stoichiometry of the reaction, in a batch reactor the number of moles of the reactants and products can be expressed in terms of the conversion of reactant A:

$$N_A = N_{A0} \cdot (1-X), \ N_B = N_{B0} - N_{A0} \cdot X, \ N_C = N_{A0} \cdot X, \ N_D = N_{D0} + N_{A0} \cdot X$$

and

$$\frac{dN_C}{dt} = N_{A0} \frac{dX}{dt}$$

where X is the conversion of A and the subscript 0 refers to the initial moles of A or D.

Thus, Eq. (6) can be written as:

$$\frac{dX}{dt} = k_1 \times \frac{(1-X) \times (N_{B0} - N_{A0} \times X) \times N_{Cat}}{V_{org}^2}$$
$$- k_{-1} \times \frac{X \times (N_{D0} + N_{A0} \times X) \times N_{Cat}}{V_{org}^2} \tag{7}$$

This model is very simple and contains only two adjustable parameters, but the problem is that it does not fit the experimental results

well. Accordingly, it seems necessary to introduce the effect of phase separation due to the presence of water into the model.

As already stated, most of the water produced in the reaction forms a second phase, to which part of the methanol and catalyst is transferred.

Thus, the moles of water involved in the reaction are those that are present in the organic phase (N_{Dorg}) and not the total water moles present in the reactor. To quantify this, the parameter q, referring to the fraction of the total water present in the organic phase, was introduced. Since water is very insoluble in oleic acid and in biodiesel the value of q should be very close to zero.

$$N_{Dorg} = q \cdot (N_{D0} + N_{A0} \cdot X) \tag{8}$$

Regarding methanol, the situation is somewhat more complex, since a distribution between the organic and aqueous phases occurs. For simplicity, here the number of moles of methanol in the organic phase (N_{Borg}) is expressed in terms of an adjustable parameter, p, which represents the fraction of total methanol present in the organic phase. The value of p depends on the methanol/acid ratio.

$$V_{org} = N_{A0} \times (1 - X) \times \frac{M_A}{\rho_A} + p \times (N_{B0} - N_{A0} \times X) \times \frac{M_B}{\rho_B} + N_{A0} \times X \times \frac{M_C}{\rho_C} + q \times (N_{D0} + N_{A0} \times X) \times \frac{M_D}{\rho_D} \approx$$
$$\approx N_{A0} \times (1 - X) \times \frac{M_A}{\rho_A} + p \times (N_{B0} - N_{A0} \times X) \times \frac{M_B}{\rho_B} + N_{A0} \times X \times \frac{M_C}{\rho_C} \tag{15}$$

$$N_{Borg} = p \cdot (N_{B0} - N_{A0} \cdot X) \tag{9}$$

Regarding the catalyst, as the water generated increases with conversion, a progressive decrease in the number of moles of the catalyst in the organic phase occurs, and a distribution of the catalyst is established between the organic and aqueous phases.

Therefore, a distribution coefficient, r, is introduced, given by:

$$r = \frac{N_{Catorg}}{V_{org}} \Big/ \frac{N_{Catwater}}{V_{water}} \tag{10}$$

where N_{Catorg} y $N_{Catwater}$ are the number of moles of catalyst in the organic and aqueous phase, respectively, and V_{water} is the volume of water.

The distribution coefficient, r, was determined experimentally by acid-base titration of the moles of DBSA in the organic and aqueous phases in an esterification reaction, and its value was determined to be 0.012. In the model it is assumed that this value is valid for all the temperatures assayed.

Moreover, at each instant the number of moles of catalyst in the organic phase plus the number of moles of catalyst in the water is equal to the initial number of moles of catalyst:

$$N_{Cat0} = N_{Catorg} + N_{Catwater} \tag{11}$$

Combining Eqs. (10) and (11) and rearranging, the following expression for N_{Catorg} can be obtained.

$$N_{Cat\,org} = \frac{r \times N_{Cat0}}{\frac{V_{water}}{V_{org}} + r} \tag{12}$$

Substituting in Eq. (6) the number of moles of water, methanol and catalyst in the organic phase, given by Eqs. (8), (9) and (12), we have:

$$\frac{dX}{dt} = \frac{k_1}{V_{org}^2} \times (1 - X) \times p \times (N_{B0} - N_{A0} \times X) \times \frac{r \times N_{Cat\,0}}{\frac{V_{water}}{V_{org}} + r}$$
$$- \frac{k_{-1}}{V_{org}^2} \times X \times q \times (N_{D0} + N_{A0} \times X) \times \frac{r \times N_{Cat\,0}}{\frac{V_{water}}{V_{org}} + r} \tag{13}$$

Table 4
Kinetic coefficients for the esterification of oleic acid with DBSA as catalyst.

$T\,(K)$	k_1 (M^{-2} min^{-1})	$k_{-1} \cdot q$ (M^{-2} min^{-1})
333	0.44	0.021
343	0.76	0.038
353	1.46	0.077

The volume of water is calculated from the moles of water in the aqueous phase:

$$V_{water} = (1 - q) \times (N_{D0} + N_{A0} \times X) \times \frac{M_D}{\rho_D} \approx (N_{D0} + N_{A0} \times X) \times \frac{M_D}{\rho_D} \tag{14}$$

where M_D and ρ_D are the molecular mass and the water density, respectively. For simplicity, q can be neglected because its value is very small in comparison with 1.

The volume of the organic phase was calculated from the number of moles of oleic acid, methanol, methyl oleate and water, in the organic phase:

where M_A, ρ_A, M_B, ρ_B, M_C y ρ_C are the molecular mass and the density of A, B and C, respectively.

The kinetic coefficients k_1 and k_{-1}, given in Table 4, were determined according to the procedure developed in detail in the Supplementary content (Section S1). The coefficient k_1 was determined using Eq. (13), from the experimental results in the initial moments of the reaction, in which the reverse reaction rate was considered to be negligible due to the low concentration of the reaction products. With this assumption, integration of the differential equation leads to a straight-line equation, from whose slope the coefficient k_1 was obtained at different temperatures. With respect to the coefficient k_{-1}, since there was no way to determine q individually the product $q \cdot k_{-1}$ was calculated from Eq. (13), from the equilibrium conversion and taking into account the values of k_1.

Now with the values of the rate constants of the forward and reverse reaction at three different temperatures it is possible to calculate the activation energy for the forward and reverse reactions through the Arrhenius equation in the form given by Eqs. (16) and (17):

$$\ln k_1 = \ln A_f - \frac{E_{af}}{RT} \tag{16}$$

$$\ln(q \times k_{-1}) = \ln(q \times A_b) - \frac{E_{ab}}{RT} \tag{17}$$

where E_{af} is the activation energy of the forward reaction, E_{ab} is the activation energy of the backward reaction, R is the gas constant, T is the absolute temperature, and A_f is the preexponential factor of the forward reaction, and A_b is the preexponential factor of the backward reaction.

According to Eqs. (16) and (17), a plot of $\ln k_1$ or $\ln(q \cdot k_{-1})$ vs. $1/T$ should give a straight line with a slope equal to $(-E_{af}/R)$ or $(-E_{ab}/R)$ and intercepts of $\ln A_f$ or $\ln(q \cdot A_b)$, and this can be used to calculate the value of the activation energy and the preexponential factor. This plot is shown in Fig. 6 and the values obtained for the different parameters are shown in Table 5. The activation energy was 58.5 kJ/mol for the forward reaction and 63.4 kJ/mol for the reverse reaction.

As can be seen in Table 6, the value of E_a for the forward reaction lies within the range of values given by several authors (Table 6) for the esterification of fatty acids with catalysts, while the value of E_a for the reverse reaction is somewhat higher. From
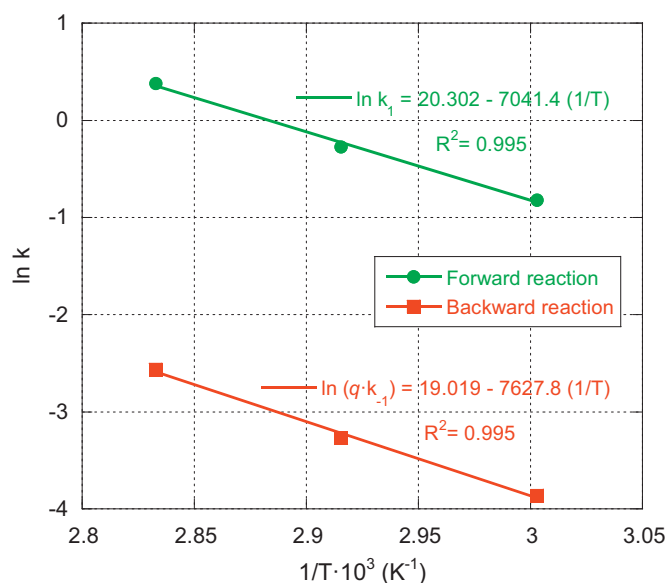
Fig. 6. Plot of $\ln k_1$ and $\ln (q \cdot k_{-1})$ vs. $1/T$ for the esterification of oleic acid with DBSA as catalyst at 60–80 °C.

Table 5
Values of the activation energy and preexponential factor for the esterification of oleic acid with DBSA as catalyst.

Reaction	Ea (kJ/mol)	A (M^{-2} min^{-1})
Forward	58.5	6.56×10^8
Backward	63.4	1.82×10^{8} [a]

[a] $q \times A_b$.

the activation energies it is possible to calculate the reaction heat as $\Delta H_r^0 = E_{af} - E_{ab} = -4.9\,kJ/mol$. This result is not very different from that calculated theoretically in Section 3.6.

Accordingly, the kinetic coefficients can be calculated from Eqs. (18) and (19):

$$k_1 = 6.56 \times 10^8 \times e^{\frac{-58.5 \times 10^3}{8.3143 \times T}} \, (M^{-2} min^{-1}) \tag{18}$$

$$k_{-1} \times q = 1.82 \times 10^8 \times e^{\frac{-63.4 \times 10^3}{8.3143 \times T}} \, (M^{-2} min^{-1}) \tag{19}$$

where T is the temperature in degrees Kelvin.

The parameter p was calculated by solving Eq. (13) with a fourth-order Runge–Kutta method for the different proportions of methanol and by minimizing the residual sum of squares (RSS) between the experimental and predicted values of the conversion of oleic acid. Thus, assuming that the value of p depends on the value of the Met factor, it was found that Eq. (20) could be used to

calculate the values of p as a function of Met (see Supplementary content, Section S2).

$$p = 1.613 \times \left(\frac{N_{B0}}{N_{A0}}\right)^{-0.77} \tag{20}$$

In conclusion, by introducing Eqs. (14), (15), (18)–(20) into Eq. (13) and solving the resulting equation by numerical methods, it is possible to predict the conversion of oleic acid under very different experimental conditions at any time. The solid lines in Figs. 2–5 represent the oleic acid conversion predicted by the model and the dots show the experimental data. The good fit between the experimental and predicted results shows the goodness of the model.

3.7. Effect of the presence of triglycerides on the esterification of oleic acid

One of the main reasons for studying the effect of the operating conditions on the kinetics and equilibrium of the esterification of oleic acid with methanol is the presence of FFAs in low-cost oils. Logically, the next step in this research was to verify that the results obtained regarding the kinetics and equilibrium of the esterification reactions were still valid when most of the reaction mixture was formed by triglycerides. For this purpose, a mixture of 85 w% of triglycerides and 15 w% of oleic acid, was used simulating the composition of an oil with high acidity.

The operating conditions were those that, according to our previous work with this catalyst [15], were considered optimum for the transesterification reaction: 80 °C, a catalyst/acid of molar ratio of 0.01:1 (equivalent to a catalyst/oil molar ratio 0.03:1) and a methanol/acid molar ratio of 2:1 (equivalent to a methanol/oil molar ratio of 6:1). These experimental conditions are shown in Table 1, experiment 26. The progress of the esterification reaction was determined by acid-base titration. The solid circles in Fig. 7 represent the experimental results.

The solid line in Fig. 7 shows the conversion of oleic acid versus time, predicted by simultaneously solving Eq. (21) for esterification and Eq. (22) for transesterification. Since both chemical reactions occur simultaneously, X_A was defined as the conversion of oleic acid and X_{TG} as the conversion of triglycerides.

Eq. (21) is derived from Eq. (13), in which the expression representing the number of moles of methanol and methyl oleate is changed, since in this case the number of moles of these compounds also varies due to the transesterification reaction. The values of the parameters k_1, $k_{-1} \cdot q$, p and r were those determined in Section 3.6.1.

Eq. (22) is derived from Eq. (8) from our previous work [15], with the following changes: (a) now, the kinetic equation is written in differential form; (b) the kinetic coefficient determined in that work has been divided by the initial concentration of catalyst in order to include the concentration of catalyst in the kinetic equation; (c) a term for the decreasing catalyst concentration has been included.

Table 6
Comparison of activation energies for the esterification of fatty acids with different acid catalysts.

Fatty acid	Catalyst	E_{af} (forward reaction) (kJ/mol)	E_{ab} (backward reaction) (kJ/mol)	Reference
Myristic acid	P-toluenesulfonic acid	47.4–58.9	25.4–45.9	[32]
Palmitic acid	P-toluenesulfonic acid	40.7	8.9	[29]
Palm fatty acids[a]	Sulfuric acid	27.3–62.9		[31]
Palm fatty acids[a]	Methanesulfonic acid	15.8–42.3		[31]
Oleic acid	Sulfuric acid	23.1		[48]
Oleic acid	Relite CFS	58.5		[34]
Oleic acid	Amberlyst 15	74.5	36.6	[49]
Oleic acid	30% SiW$_{12}$/Hβ	49.8		[50]
Oleic acid	Fe–Zn double-metal cyanide	52.8		[51]
Mixture[b]	Sulfuric acid	44.6–50.7	31.0–42.8	[26]

[a] Lauric (1.2%), myristic (0.1%), palmitic (46.4%), oleic (41.2%) and linoleic (11.1%) acid.
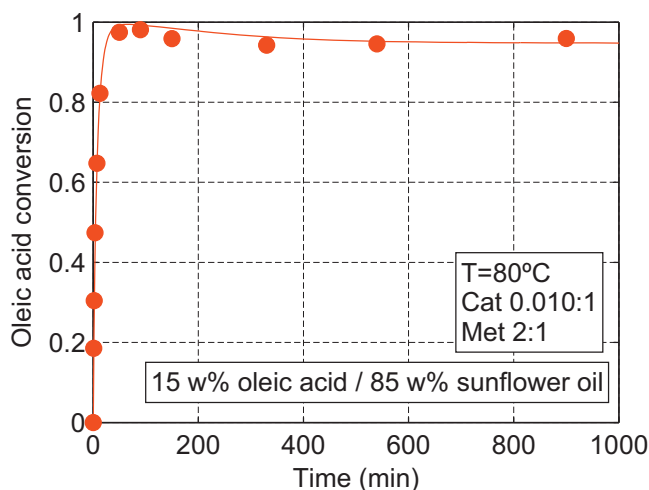[b] Palmitic (6%), stearic (3%), oleic (17%) and linoleic (72%) acid.

Fig. 7. Kinetics of the esterification of oleic acid, with DBSA as catalyst in the presence of triglycerides.

Evidently, the expression for V_{org} was also modified, adding the term corresponding to triglycerides (Eq. (23)):

$$\frac{dX_A}{dt} = \frac{k_1}{V_{org}^2} \times (1 - X_A) \times p \times (N_{B0} - N_{A0} \times X_A - 3 \times N_{TG0} \times X_{TG}) \times \frac{r \times N_{Cat0}}{\frac{V_{water}}{V_{org}} + r}$$
$$- \frac{k_{-1}}{V_{org}^2} \times \frac{(N_{A0} \times X_A + 3 \times N_{TG0} \times X_{TG})}{N_{A0}} \times q \times (N_{D0} + N_{A0} \times X_A) \times \frac{r \times N_{Cat0}}{\frac{V_{water}}{V_{org}} + r} \quad (21)$$

$$\frac{dX_{TG}}{dt} = \frac{k}{V_{org}} \times (1 - X_{TG}) \times \frac{r \times N_{Cat0}}{\frac{V_{water}}{V_{org}} + r} \quad (22)$$

$$V_{org} = N_{A0} \times (1 - X_A) \times \frac{M_A}{\rho_A} + p \times (N_{B0} - N_{A0} \times X_A - 3 \times N_{TG0} \times X_{TG}) \times \frac{M_B}{\rho_B}$$
$$+ (N_{A0} \times X_A + 3 \times N_{TG0} \times X_{TG}) \times \frac{M_C}{\rho_C} + N_{TG0} \times (1 - X_{TG}) \times \frac{M_{TG}}{\rho_{TG}} \quad (23)$$

Fig. 7 shows that: (a) the time required for the esterification of oleic acid to reach maximum conversion was only about 1 h, whereas it took 6 h, under the same operating conditions, for pure triglyceride conversion to reach 97.6% [15], (b) the equilibrium conversion of oleic acid mixed with triglycerides was similar to that obtained in previous sections for the esterification of pure oleic acid; (c) the esterification reaction of oleic acid in triglycerides initially reaches a conversion close to 100% and then decreases until it stabilizes at the same conversion as the reaction without triglycerides. This decrease in the conversion of oleic acid is probably due to the shift in the reaction equilibrium brought about by the large amount of biodiesel formed in the transesterification reaction. However, this decrease is not very marked because it is probably compensated by the simultaneous displacement of the reaction to the right due to the separation of water from the reaction mixture.

The first conclusion related to the experimental results obtained is that under the same operating conditions the esterification of fatty acids takes place in a considerably shorter time than the transesterification of triglycerides, showing that this catalyst can be used to obtain biodiesel from raw materials with a high proportion of FFAs in a single step. It may also be concluded that the equilibrium conversion reached in the esterification of fatty acids is independent of the presence of triglycerides.

With respect to the kinetic model obtained in this work, it was found that not only can it be applied to the esterification of pure oleic acid but that it can also be applied when the esterification of oleic acid takes place in the presence of triglycerides.

4. Conclusions

The esterification of oleic acid with methanol using 4-dodecylbenzenesulfonic acid as catalyst was studied. Taking into account that DBSA is an excellent catalyst in transesterification reactions and, more importantly, that this catalyst has a proven capacity to catalyze both esterification and transesterification reactions simultaneously, a thorough investigation of the esterification of oleic acid with this catalyst was conducted to generate the necessary information for the design of processes for obtaining biodiesel from raw materials with high contents of FFAs and water.

First, a comparative study of the catalytic activity of DBSA and other catalysts commonly used in the esterification of fatty acids, such as sulfuric acid, p-TSA and several solids with acid sulfonic groups, was performed. The conclusion was that the reaction rate increases with increasing hydrophobicity of the catalyst, indicating that not only does DBSA have a much higher catalytic activity in the transesterification of triglycerides than other acid catalysts, but also that it exerts a higher catalytic activity in the esterification of fatty acids.

The second and main objective of this work was to study the influence of the operating conditions on the kinetics and on the equilibrium of the esterification of oleic acid with DBSA as catalyst.

The main conclusions regarding the kinetics of the reaction are: (a) the temperature and catalyst/fatty acid molar ratio has a positive effect on the kinetics, i.e., an increase in either of these factors leads to an increase in the reaction rate; (b) the methanol/fatty acid molar ratio has an almost negligible effect on the kinetics; (c) the initial water/fatty acid weight ratio has a negative effect on the kinetics, i.e., the higher the initial proportion of water in the oleic acid, the slower the reaction rate. This effect can be attributed to the formation of an aqueous phase, which removes part of the catalyst and hence reduces the concentration of catalyst in the organic phase and therefore the reaction rate.

Regarding the reaction equilibrium, it was found that: (a) while the proportion of catalyst does not influence the equilibrium conversion, an increase in the temperature decreases it, although very slightly, suggesting that the reaction is slightly exothermic; (b) the higher the initial proportion of methanol, the higher the equilibrium conversion, although the increase was found to be almost negligible when the proportions of methanol were higher than 2. Accordingly, the conclusion is that the addition of high proportions of methanol to displace the equilibrium to obtain conversions close to 100% is not necessary; (c) the initial water/fatty acid weight ratio had a negligible effect on the equilibrium conversion.

The kinetics of the esterification of oleic acid was also studied, and a reversible second-order model was developed that includes the effect of the separation of the aqueous phase from the reaction mixture and hence also the progressive decrease in the concentration of catalyst, methanol, and volume of the reaction mixture. This kinetic model adequately predicts the conversion of oleic acid versus time across a wide range of operation conditions, including different reaction temperatures, proportions of catalyst, methanol and initial water. The activation energy was 58.5 kJ/mol for the forward reaction and 63.4 kJ/mol for the reverse reaction.

Finally, an experiment addressing the esterification of oleic acid in a mixture with triglycerides was carried out, and it was found that: (a) the esterification of fatty acids takes place in a considerably shorter time than the transesterification of triglycerides; b) the kinetic model obtained in this work is also able to adequately predict the kinetics of the esterification of oleic acid in the presence of triglycerides.

The final conclusion is that DBSA appears to be an excellent single-step catalyst to obtain biodiesel from raw materials with a high proportion of FFAs.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015.05.057

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